

## REMARKS

Reconsideration and allowance of the subject application are respectively requested.

Claims 1-65 are pending in the present application. Claims 1, 2, 10, 11, 12 and 65 are independent.

The Examiner rejected Claims 1-65 under 35 U.S.C. §112 (first paragraph). This rejection is traversed. Reconsideration is requested in light of the following remarks.

To substantiate the rejection, the Examiner made the following statement concerning Claims 1-65:

“ ... the specification, while being enabling for the dendritic macromolecules particularly defined in the referenced copending U.S. patent application S.N. 60/221,512, does not reasonably provide enablement for all dendritic macromolecules”.

In reply, Applicants submit that, contrary to the Examiner's assertion, in Claims 1-65, when reference is made to dendritic macromolecules, such macromolecules are those described in copending United States patent application S.N. 60/221,512 (copy enclosed for the Examiner's convenience). On page 6 of the outstanding Official Action, the Examiner states that the present application lacks further definition of the term “dendritic macromolecule” to limit the interpreted scope in its instant use to anything less than the broad meaning of the term. The Examiner goes on to state that the disclosure of the copending '512 application may be used to define dendritic macromolecules in the claims, “ ... but the limitations will also need to be inserted into the specification at the appropriate location”. It is this last point where Applicants believe confusion exists.

Enclosed herewith is a copy of the '512 application.

As the Examiner will see, the discussion of the dendritic macromolecule in the '512 application is in line with the discussion of the "sub-group" of dendritic macromolecules useful in invention defined by present Claims 1-65. In other words, the limitation which the Examiner believes necessary to be extracted from the '512 application and inserted in the present application to define the sub-group of the dendritic macromolecules already exists in the present application. For example, compare the description of the dendritic macromolecule in the '512 application at page 5, lines 1-3 with the definition of the dendritic macromolecule in Claim 1 of the present application.

Applicants submit that the present application clearly contains sufficient specification of the sub-group of dendritic macromolecules referred to in the claims of the present application.

Thus, Applicants submit that the term "dendritic macromolecule" as used in the claims of the present application does not encompass all such molecules but is related to the sub-group of dendritic macromolecules discussed in the present application and the '512 application.

Accordingly, Applicants submit that Claims 1-65 are of a scope commensurate with the present specification. The Examiner is requested to reconsider and withdraw the rejection Claims 1-65 under 35 U.S.C. §112 (first paragraph).

The Examiner rejected Claims 1-65 under 35 U.S.C. §103(a) as being purportedly unpatentable over United States patent 6,316,514 [Falke, et al. (Falke)] in view of United States patent 6,114,458 [Hawker, et al. (Hawker)]. This rejection is traversed. Reconsideration is requested in light of the following remarks.

It is believed the prior art rejection will fall in light of the following comments above. Notwithstanding this, Applicants refer the Examiner to the Examples of the '512 application enclosed herewith which clearly illustrate that the sub-group of dendritic

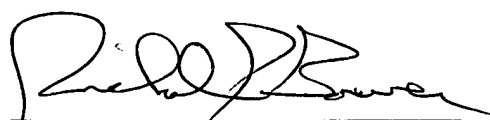
macromolecules referred to in the present claims has significantly improved solubility characteristics compared with conventional dendritic macromolecules such as those referred to in Hawker. As stated in the paragraph bridging pages 3 and 4 of the '512 application, the prior art dendritic macromolecules are difficult to handle when producing commercial quantities of isocyanate-based foam due to their relatively poor solubility in polyether polyols at high active hydrogen functionality and molecular weight.

The Examiner is requested to reconsider and withdraw the rejection under 35 U.S.C. §103(a).

In view of the above comments and remarks, it is believed that the present application is now in condition for allowance, and a Notice thereof is respectively requested.

Applicants' undersigned attorney may be reached in our Washington, D.C. office by telephone at (202) 625-3500. All correspondence should continue to be directed to our address given below.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Richard P. Bauer', written over a horizontal line.

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# PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 C.F.R. § 1.53(c).

DOCKET  
NUMBER

1960.207 PV

Type a plus  
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## TITLE OF THE INVENTION (280 characters max)

DENDRITIC MACROMOLECULES WITH IMPROVED POLYETHER  
POLYOL SOLUBILITY AND PROCESS FOR PREPARATION THEREOF

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## ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification Number of Pages 29 ☐ Small Entity Statements

☒ Drawings Number of Sheets 1 ☐ Other (specify) \_\_\_\_\_

## METHOD OF PAYMENT (check one)

☐ A check or money order is enclosed to cover the Provisional filing fees

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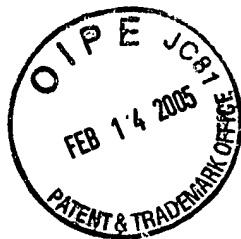
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\$150.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

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**Gowlings Ref: T846586US**

**FINAL VERSION**

**Applicants/Inventors:** Bo Pettersson  
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**Title: Dendritic Macromolecules With Improved Polyether Polyol Solubility and Process for Preparation Thereof**

**Assignee:** Perstorp AB

**JURISDICTION:** United States - Provisional  
**DATE:** July 28, 2000

DATE: July 28, 2000

INTELLECTUAL PROP. 1247355\_1

## BACKGROUND OF THE INVENTION

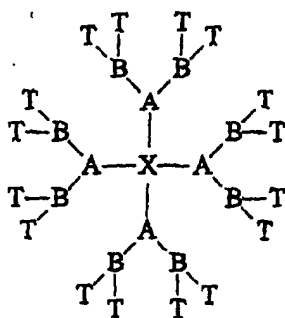
### FIELD OF THE INVENTION

In one of its aspects, the present invention relates to a hyperbranched macromolecule having a dendritic or near dendritic structure. Preferably, the macromolecule comprises a central epoxide nucleus from which chain extenders form a branched structure corresponding to at least one generation (as defined below). In a preferred embodiment, the macromolecule is terminated by means of at least one chain stopper. In another of its aspect, the present invention relates to a process for production of the subject hyperbranched macromolecule.

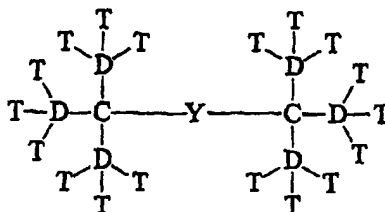
### DESCRIPTION OF THE PRIOR ART

Hyperbranched and dendritic macromolecules (also referred to herein as "dendrimers") can generally be described as three dimensional highly branched molecules having a tree-like structure. Dendrimers generally are highly symmetric, while similar macromolecules designated as hyperbranched macromolecules may, to a certain degree, hold an asymmetry, yet maintaining the highly branched tree-like structure. Dendrimers can be said to be monodisperse variations of hyperbranched macromolecules. Hyperbranched and dendritic macromolecules normally consist of an initiator or nucleus having one or more reactive sites and a number of surrounding branching layers and, optionally, a layer of chain terminating molecules. The layers are usually called "generations", a designation used throughout this specification.

The composition of hyperbranched dendritic or near dendritic macromolecules having three generations can be illustrated by below Formulae (I) and (II):



Formula (I)



Formula (II)

10

wherein:

X and Y are an initiator or nucleus having four and two reactive sites, respectively;

A, B, C and D are chain extenders having three (A and B) and four (C and D) reactive sites, each extender forming one generation in the macromolecule; and

T is a terminating chain stopper forming the third and last generation.

T may either be monofunctional or give a suitable terminal functionality, consisting for instance of hydroxyl, carboxyl or epoxide groups, to the macromolecule.

T may also be a moiety of a saturated or unsaturated compound, such as an air drying fatty acid or a derivative thereof.

As a result of their symmetrical or near symmetrical highly branched structure, hyperbranched macromolecules of the polyester type are characterized by having useful advantages over ordinary polyesters. Hyperbranched macromolecules exhibit a low polydispersity especially in comparison to branched, but also linear, polyesters. A hyperbranched macromolecule can, due to its structure, be designed to give a very high molecular weight and yet exhibit a very low viscosity, thus being suitable as component in compositions such as coatings and the like in order to increase the solid content.

Various dendritic macromolecules are, inter alia, described:

Tomalia et al in Angew. Chem. Int. Ed. Engl. 29 pages 138-175 (1990);  
United States patent 5,418,301 [Hult et al (Hult)];



Tomalia et al discloses the preparation of polyamide amines of the dendrimer  
5 type.  $\text{NH}_2$  is used as the initiator molecule, and methyl acrylate and ethylene diamine  
as the chain extenders. The resultant macromolecules are  $\text{NH}_2$  terminated. Chain  
stoppers are not used.

Hult discloses a dendritic macromolecule of the polyester type. The  
macromolecule includes as central initiator molecule or initiator polymer a compound  
10 having one or more reactive hydroxyl groups and as chain extender a hydroxyfunctional  
carboxylic acid having at least one carboxyl group and at least two hydroxyl groups.

Sørensen discloses a hyperbranched macromolecule of the polyester type  
comprising a central monomeric or polymeric nucleus and at least one generation of a  
branching chain extender having at least three reactive sites of which at least one is a  
15 hydroxyl or hydroxyalkyl substituted hydroxyl group and at least one is a carboxyl or  
terminal epoxide group. The nucleus is an epoxide compound having at least one  
reactive epoxide group. The macromolecules disclosed by Sørensen are particularly  
advantageous in that they enhance various film properties (drying time, hardness and  
scratch resistance) of a coating composition in which they are used.

20 The macromolecules of Hult and Sørensen are stated as being useful in a  
number of applications, including in the preparation of products constituting or being  
part of alkyds, alkyd emulsions, saturated polyesters, unsaturated polyesters, epoxy  
resins, phenolic resins, polyurethane resins, polyurethane foams and elastomers,  
binders for radiation curing systems such as systems cured with ultraviolet (UV) and  
25 infrared (IR) light or electron-beams (EB), dental materials, adhesives, synthetic  
lubricants, microlithographic coatings and resists, binders for powder systems, amino  
resins, composites reinforced with glass, aramid or carbon/graphite fibres and  
moulding compounds based on urea-formaldehyde resins, melamine-formaldehyde  
resins or phenol-formaldehyde resins.

30 While the macromolecules of Hult and Sørensen are significant advances in the  
art, there is still room for improvement, particularly in the application of the

macromolecules in isocyanate-based foams, such as polyurethane foams. Specifically, the specific macromolecules taught by Hult and Sørensen are difficult to handle when producing commercial quantities of isocyanate-based foam, such as polyurethane foam. The principal reason for this is the relatively poor solubility in polyether polyols of the macromolecules at high active hydrogen functionality and molecular weight.

Accordingly, it would be highly desirable to have a convenient means for incorporation of dendritic macromolecules in a polyurethane foam matrix. More particularly, it would be very advantageous to be able to incorporate into the polyurethane foam matrix a dendritic macromolecule having a combination of high active hydrogen content, high active hydrogen functionality and which may be readily processed in a polyurethane foam production facility.

### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a novel dendritic macromolecule which obviates or mitigates at least one of the above-mentioned disadvantages of the prior art.

Accordingly, in one of its aspects, the present invention provides a dendritic macromolecule having the following characteristics:

- (i) an active hydrogen content of greater than about 3.8 mmol/g;
- (ii) an active hydrogen functionality of at least about 8; and
- (iii) at least a 15% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number less than about 40 mg KOH/g to form a stable liquid at 23°C.

Accordingly, the present inventors have discovered a novel group of dendritic macromolecules which may be conveniently incorporated in polyurethane foam. Surprisingly and unexpectedly, it has been further discovered that the novel group of dendritic macromolecules confer significant load building properties to the polyurethane foam matrix and may be used for this purpose to partially or fully displace current relatively expensive chemical systems which are used to confer load building characteristics to polyurethane foam. This effect will be illustrated below in the Examples section.

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A feature of the present dendritic macromolecule is that at least a 15% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number less than about 40 mg KOH/g to form a stable liquid at 23°C. As used throughout this specification, the term "stable liquid", when used in connection with the solubility characteristics of the dendritic macromolecule, is intended to mean that the liquid formed upon mixing the dendritic macromolecule and the polyol has a substantial constant light transmittance (transparent at one extreme and opaque at the other extreme) for at least 2 hours, preferably at least 30 days, more preferably a number of months, after production of the mixture. Practically, in one embodiment, the stable liquid will be in the form a clear, homogeneous liquid (e.g., a solution) which will remain as such over time. In another embodiment, the stable liquid will be in the form an emulsion of (at least a portion of) the dendritic macromolecule in the polyol which will remain as such over time - i.e., the dendritic macromolecule will not settle out over time.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present invention will be described with reference to the accompanying Figure in which there is illustrated a solubility profile for the dendritic macromolecules produced in Examples 4-6 discussed hereinbelow.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Thus, the present inventors have discovered a novel group of dendritic macromolecules which have surprising and unexpected utility in the production of isocyanate-based polymer foams such as polyurethane foams. Specifically, it has been discovered that the present dendritic macromolecules surprisingly and unexpectedly improve various properties of polyurethane foams such as the load bearing properties and/or allow for replacement of the relatively expensive copolymer polyols currently used to build load in polyurethane foams.

As stated above, the present dendritic macromolecules are characterized by:

- (i) an active hydrogen content of greater than about 3.8 mmol/g;
- (ii) an active hydrogen functionality of at least about 8; and

(iii) at least a 15% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number less than about 40 mg KOH/g to form a stable liquid at 23 °C.

As used throughout this specification, the term "active hydrogen functionality" is intended to mean the number of active hydrogen moieties per molecule of the dendritic macromolecule.

The general architecture of the present dendritic macromolecules is similar to other such macromolecules.

Specifically, the present dendritic macromolecules may be derived from: (a) a central monomeric or polymeric nucleus, (b) at least one generation of a branching monomeric or polymeric chain extender have a plurality of reactive sites comprising an active hydrogen-containing moiety, and (c) optionally, at least one monomeric or polymeric chain stopper which serves to terminate the macromolecule.

The central monomeric or polymeric nucleus included in the hyperbranched macromolecule is not particularly restricted and, in a preferred embodiment, is suitably selected from the groups of central monomeric or polymeric initiators disclosed in Hult and Sörensen referred to above and the contents of each of which are hereby incorporated by reference.

The chain extender(s) included in the hyperbranched macromolecule is not particularly restricted and, in a preferred embodiment, is suitably selected from the groups of chain extenders disclosed in Hult and Sörensen referred to above and the contents of each of which are hereby incorporated by reference.

The chain stopper, if used in the hyperbranched macromolecule is not particularly restricted and, in a preferred embodiment, is suitably selected from the groups of chain stoppers disclosed in Hult and Sörensen referred to above and the contents of each of which are hereby incorporated by reference.

The present dendritic macromolecules may be of the so-called ester type, for example, as described by Hult and Sörensen. Alternatively, the present dendritic macromolecules may be of the so-called ether type, for example, as described by Magnusson et al. in *Macromol. Rapid Commun.* 20, 453-457 (1999).

Further, the dendritic macromolecule need not necessarily include a central monomeric or polymeric initiator. Specifically, the macromolecule may be a polymer derived directly from the chain extender(s) - this will be illustrated in Example 7.

As will be developed hereinbelow in the Examples (see particularly Example 7), it is possible to select the chain extender to achieve a dendritic macromolecule having solubility parameter (iii) set out above, without the need for the use of a chain stopper.

Embodiments of the present invention will be described with reference to the following Examples which are provided for illustrative purposes only and should not be used to construe or limit the scope of the invention.

#### Example 1

100.0 kg of an alkoxyated pentaerythritol (Perstorp Specialty Chemicals) with a hydroxyl value of 630 mg KOH/g, 1055 kg of 2,2-dimethylolpropionic acid (Bis-MPA, Perstorp Specialty Chemicals) and 8.5 kg of paratoluenic sulphonic acid were cold mixed in a reactor equipped with a heating system with accurate temperature control, a mechanical stirrer, a pressure gauge, a vacuum pump, a cooler, nitrogen inlet and a receiver. The mixture was heated carefully during slow stirring to a temperature of 140°C. Slow stirring of the mixture at this temperature was maintained at atmospheric pressure until all 2,2-dimethylolpropionic acid was dissolved and the reaction mixture formed a fully transparent solution. The stirring speed was then significantly increased and vacuum was applied to a pressure of 30 mbar. Reaction water immediately started to form, which was collected in the receiver. The reaction was allowed to continue for a further 7 hours, until a final acid value of 8.9 mg KOH/g was obtained. This corresponded to a chemical conversion of ~98%.

The obtained dendritic polymer had the following characteristics:

Final acid value:	8.9 mg KOH/g
Final hydroxyl value:	489 mg KOH/g
Peak molecular weight:	3490 g/mole
Mw (SEC):	3520 g/mole

Mn (SEC): 2316 g/mole

PDI (Mw/Mn): 1.52

Average hydroxyl functionality: 30.4 OH-groups/molecule

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The obtained properties were in good agreement with the expected theoretical molecular weight of 3607 g/mole at 100% chemical conversion and a theoretical hydroxyl value of 498 mg KOH/g, which would correspond to a OH-functionality of 32.

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#### Example 2

16.7 kg of an alkoxyated pentaerythritol with a hydroxyl value of 630 mg KOH/g, 375 kg of 2,2-dimethylolpropionic acid (Bis-MPA, Perstorp Specialty Chemicals) and 3.0 kg of paratoluenic sulphonic acid were cold mixed in a reactor equipped with a heating system with accurate temperature control, a mechanical stirrer, a pressure gauge, a vacuum pump, a cooler, nitrogen inlet and a receiver. The mixture was heated carefully during slow stirring to a temperature of 140°C. Slow stirring of the mixture at this temperature was maintained at atmospheric pressure until all 2,2-dimethylolpropionic acid was dissolved and the reaction mixture formed a fully transparent solution. The stirring speed was then significantly increased and vacuum was applied to a pressure of 30 mbar. Reaction water immediately started to form, which was collected in the receiver. The reaction was allowed to continue for a further 8 hours, until a final acid value of 11.9 mg KOH/g was obtained. This corresponded to a chemical conversion of ~97%.

25

The obtained dendritic polymer had the following characteristics:

Final acid value: 11.9 mg KOH/g

Final hydroxyl value: 481 mg KOH/g

Peak molecular weight: 5110 g/mole

30

Mw (SEC): 5092 g/mole

Mn (SEC): 3041 g/mole

PDI (Mw/Mn):

1.67

Average hydroxyl functionality: 43.8 OH-groups/molecule

5 The obtained properties were in good agreement with the expected theoretical molecular weight of 7316 g/mole at 100% chemical conversion and a theoretical hydroxyl value of 491 mg KOH/g, which would correspond to a OH-functionality of 64.

10 Example 3

83.6 kg of an alkoxyated pentaerythritol with a hydroxyl value of 630 mg KOH/g, 375.0 kg of 2,2-dimethylolpropionic acid (Bis-MPA, Perstorp Specialty Chemicals) and 3.25 kg of paratoluenic sulphonic acid were cold mixed in a reactor equipped with a heating system with accurate temperature control, a mechanical stirrer, a pressure gauge, a vacuum pump, a cooler, nitrogen inlet and a receiver. The mixture was heated carefully during slow stirring to a temperature of 140°C. Slow stirring of the mixture at this temperature was maintained at atmospheric pressure until all 2,2-dimethylolpropionic acid was dissolved and the reaction mixture formed a fully transparent solution. The stirring speed was then significantly increased and vacuum was applied to a pressure of 30 mbar. Reaction water immediately started to form, which was collected in the receiver. The reaction was allowed to continue for a further 7.5 hours, until a final acid value of 6.0 mg KOH/g was obtained. This corresponded to a chemical conversion of ~98%.

The obtained dendritic polymer had the following characteristics:

Final acid value:	4.7 mg KOH/g
Final hydroxyl value:	508 mg KOH/g
Peak molecular weight:	1998 g/mole
Mw (SEC):	1997 g/mole
Mn (SEC):	1451 g/mole
PDI (Mw/Mn):	1.37

Average hydroxyl functionality: 18 OH-groups/molecule

The obtained properties were in good agreement with the expected theoretical molecular weight of 1750 g/mole at 100% chemical conversion and a theoretical hydroxyl value of 513 mg KOH/g, which would correspond to a OH-functionality of 16.

#### Example 4

25.0 kg of the dendritic polymer according to Example 1, 8.4 kg of an aliphatic acid with nine carbons with an acid value of 363 mg KOH/g and 3.3 kg of xylene were charged to a reactor equipped with a heating system with accurate temperature control, a mechanical stirrer, a pressure gauge, a vacuum pump, a dean-stark device for azeotropic removal of water, a cooler, nitrogen inlet and a receiver. The mixture was heated under stirring with a nitrogen flow of 500-600 l/h through the reaction mixture from room temperature up to 170°C. At this temperature all xylene was refluxing and the reaction water which started to form was removed by azeotropic distillation. The reaction was allowed to continue for a further 1.5 hours at 170°C, after which the reaction temperature was increased to 180°C. The reaction mixture was kept at this temperature for a further 2.5 hours until an acid value of 5.7 mg KOH/g was obtained. Full vacuum was then applied to the reactor to remove all xylene from the final product.

The obtained derivatized dendritic polymer had the following characteristics:

Final acid value:	6.2 mg KOH/g
Final hydroxyl value:	293 mg KOH/g
Peak molecular weight:	4351 g/mole
Mw (SEC):	4347 g/mole
Mn (SEC):	1880 g/mole
PDI (Mw/Mn):	2.31

Average hydroxyl functionality: 22.7 OH-groups/molecule



The obtained properties were in good agreement with the expected theoretical molecular weight of 4699 g/mole at 100% chemical conversion and a theoretical hydroxyl value of 287 mg KOH/g, which would correspond to a OH-functionality of 24.

#### Example 5

25.0 kg of the dendritic polymer according to Example 3, 5.25 kg of an aliphatic acid with nine carbons with an acid value of 363 mg KOH/g and 3.0 kg of xylene were charged to a reactor equipped with a heating system with accurate temperature control, a mechanical stirrer, a pressure gauge, a vacuum pump, a dean-stark device for azeotropic removal of water, a cooler, nitrogen inlet and a receiver. The mixture was heated under stirring with a nitrogen flow of 500-600 l/h through the reaction mixture from room temperature up to 180°C. At this temperature all xylene was refluxing and the reaction water which started to form was removed by azeotropic distillation. The reaction was allowed to continue for a further 5 hours at 180°C until an acid value of 6.0 mg KOH/g was reached. Full vacuum was then applied to the reactor to remove all xylene from the final product.

The obtained derivatized dendritic polymer had the following characteristics:

Final acid value:	6.0 mg KOH/g
Final hydroxyl value:	360 mg KOH/g
Peak molecular weight:	2700 g/mole
Mw (SEC):	2733 g/mole
Mn (SEC):	1673 g/mole
PDI (Mw/Mn):	1.61

Average hydroxyl functionality: 17.3 OH-groups/molecule

The obtained properties were in reasonable agreement with the expected theoretical molecular weight of 2080 g/mole at 100% chemical conversion and a

theoretical hydroxyl value of 367 mg KOH/g, which would correspond to a OH-functionality of 13.6.

#### Example 6

5        25.0 kg of the dendritic polymer according to Example 2, 8.3 kg of an aliphatic acid with nine carbons with an acid value of 363 mg KOH/g and 3.3 kg of xylene were charged to a reactor equipped with a heating system with accurate temperature control, a mechanical stirrer, a pressure gauge, a vacuum pump, a dean-stark device for azeotropic removal of water, a cooler, nitrogen inlet and a receiver. The mixture was  
10    heated under stirring with a nitrogen flow of 500-600 l/h through the reaction mixture from room temperature up to 180°C. At this temperature all xylene was refluxing and the reaction water which started to form was removed by azeotropic distillation. The reaction was allowed to continue for a further 5 hours at 180°C until an acid value of 6.8 mg KOH/g was reached. Full vacuum was then applied to the reactor to remove all  
15    xylene from the final product.

The obtained derivatized dendritic polymer had the following characteristics:

Final acid value:	6.8 mg KOH/g
Final hydroxyl value:	280 mg KOH/g
20    Peak molecular weight:	5274 g/mole
Mw (SEC):	5245 g/mole
Mn (SEC):	2428 g/mole
PDI:	2.16

25        The obtained properties were in reasonable agreement with the expected theoretical hydroxyl value of 283mg KOH/g.

#### Example 7

30        200.0 g of trimethylolpropane oxetane (TMPO, Perstorp Specialty Chemicals) was charged to a reactor equipped with a mechanical stirrer, a cooler and a heating system with adequate heating control. 2.0 g of a solution of BF<sub>3</sub> etherate (10% in

diethylether) was charged at room temperature to the reactor during less than 120 seconds. A strong exotherm was seen as a result of the ring opening polymerization of the oxetane monomer. Once the exotherm faded, the reaction mixture was heated to 150°C and kept at that temperature under stirring for a further 90 minutes. The reaction mixture was then cooled to room temperature at which the final product was recovered.

The obtained dendritic polymer of polyether type had the following characteristics:

Final hydroxyl value:	500 mg KOH/g
Peak molecular weight:	6307 g/mole
Mw (SEC):	5309 g/mole
Mn (SEC):	2011 g/mole
PDI:	2.64

Average hydroxyl functionality: 56 OH-groups/molecule

Chemical conversion: 99.4% with regard to residual monomer content

#### Example 8

The solubility of each of the dendritic polymers according to Examples 1-3 in a glycerol based polyether polyol with an hydroxyl value of 32 mg KOH/g was evaluated.

15.0 g of the respective dendritic polymer according to Examples 1-3 was added to a beaker containing 75.0 g of a glycerol based polyether polyol with a hydroxyl value of 32 mg KOH/g. The mixture was heated under stirring to 120°C during 30 minutes and then allowed to cool down to room temperature. The ability for each dendritic polymer to form a stable solution with the polyether polyol was evaluated after 120 minutes.

None of the dendritic polymers according to Examples 1-3 were able to form a stable solution with the glycerol-based polyether polyol of hydroxyl value 32 mg

KOH/g. The dendritic polymers according to Examples 1-3 partly precipitated from the solution and this could be observed in the form of a separate phase at the bottom of the beaker.

5 Example 9

The solubility of each of the dendritic polymers according to Examples 4-6 in a glycerol based polyether polyol with an hydroxyl value of 32 mg KOH/g was evaluated.

10 15.0 g of the respective dendritic polymer according to Examples 4-6 was added to a beaker containing 75.0 g of a glycerol based polyether polyol with a hydroxyl value of 32 mg KOH/g. The mixture was heated under stirring to 120°C during 30 minutes and then allowed to cool down to room temperature. The ability for each dendritic polymer to form a stable solution with the polyether polyol was evaluated after 120 minutes.

15 All of the evaluated dendritic polymers according to Examples 4-6 were fully soluble in the glycerol based polyether polyol. Fully transparent solutions were obtained in all cases, which were stable over time. Due to the excellent solubility, samples of higher concentrations based on the products obtained according to Examples 4-6. These were then evaluated with regard to viscosity at 23°C. Samples of different  
20 concentrations of dendritic polymer according to Examples 4-6 in polyether polyol were prepared and found to be fully compatible with the base glycerol based polyether polyol. These stable solutions remained as such even after 30 days.

25 The attached Figure illustrates the viscosity dependence in a polyether polyol of the products according to Examples 4-6. As can be seen from the results illustrated in the attached Figure, very good solubility behaviour of the products according to Examples 4-6 were obtained.

Example 10

30 The solubility of the dendritic polymer of polyether type according to Example 7 in a glycerol based polyether polyol with an hydroxyl value of 32 mg KOH/g was evaluated.

15.0 g of the dendritic polymer according to Example 7 was added to a beaker containing 75.0 g of a glycerol based polyether polyol with a hydroxyl value of 32 mg KOH/g. The mixture was heated under stirring to 120°C during 30 minutes and then allowed to cool down to room temperature. The ability for the product according to Example 7 to form a stable solution with the polyether polyol was evaluated after 120 minutes.

It was found that the dendritic polymer of polyether type according to Example 7 formed an opaque but completely stable solution with the glycerol based polyether polyol.

#### Example 11 - Synthesis of Amine-terminated Dendritic Polymer of Polyether Type

An amine terminated dendritic polymer of polyether type is prepared according to the following principal synthesis procedure:

- Step 1: A dendritic polymer of polyether type according to Example 7 and a suitable solvent such as tetrahydrofuran (THF) are charged to a reactor equipped with a mechanical stirrer, a heating system with adequate temperature control, a cooler, gas inlet, a vacuum pump and a receiver. When a transparent solution has been obtained, NaOH or KOH or NaH are added in stoichiometric amount or with a slight excess, at which the dendritic alkolate is formed ( $\text{RO}^-\text{Na}^+$ ).
- Step 2: Acrylonitrile is added in a stoichiometric amount with regard to the moles of  $\text{RO}^-\text{Na}^+$  species present in the reaction mixture from Step 1. The alkolated species will then undergo an addition to the unsaturation of the acrylonitrile. The obtained product in Step 2 has therefore been converted to a nitrile terminated dendritic polymer of polyether type.
- Step 3: The nitrile functionality of the reaction product according to Step 2 is converted to primary amines by: (i) reducing the pH of the reaction solution by adding protons to the solution, (ii) thereafter passing  $\text{H}_2$  (g)

through the reaction mixture in the presence of a reducing catalyst such as Pt, Pd or Raney Ni neat or fixated (e.g., to a carbon carrier); and (iii) thereafter recovering the obtained amine functional dendritic polymer of polyether type by conventional washing and extraction procedures.

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Further details on specifics of these reaction steps may be found in House, H.O., Modern Synthetic Reactions, 16-19, Benj. Cum. Publ. (1972).

Example 12 - Amine-terminated Dendritic Polymer of Polyester Type

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A fully or partially-amine terminated dendritic polymer of polyester type according to any of the Examples 1-6 is prepared according to the following principal synthesis procedure:

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Step 1: A dendritic polymer of polyester type according to any of the Examples 1 -6, acrylic acid in a ratio COOH:OH of [0.1:1] to [1:1] with regard to the hydroxyl value of the dendritic polymer and a protonic acid such as methane sulphonic acid (~ 1 wt% concentration of the total solution), one or several inhibitors for radical polymerisation (e.g., MIHQ or HQ) and a solvent such as toluene or a mixture of, for example, toluene and THF, are charged to a reactor equipped with a mechanical stirrer, a dean-stark separator, adequate temperature control, nitrogen inlet, a cooler and a receiver. The reaction mixture is heated to 100 - 130°C, typically 110 - 120°C, at which point the solvent is starting to reflux and water is starting to form. The reaction is allowed to continue at said temperature until a low acid value of 5 - 30 mg KOH/g is reached, preferably 5-15 mg KOH/g. The product is then used as such or further purified by either washing with a weak aqueous solution of NaOH, or the residual acrylic acid is precipitated with, for example, Al<sub>2</sub>O<sub>3</sub>.

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Step 2: The acrylated product according to Step 1 is then reacted with a primary aliphatic, cycloaliphatic or aromatic amine such as propyl amine,

isopropyl amine, octyl amine, butyl amine (n, sec, tert) or benzyl amine. The amine of choice is added in stoichiometric amount or in excess to the acrylated product of Step 1, at which an addition reaction to the unsaturation of the dendritic acrylate will occur. The reaction is either performed at room temperature or a slightly elevated temperatures such as 50°C. The conversion of acrylate to amine is either followed by IR or NIR by the disappearance of acrylate unsaturations, or by GC-analysis of the residual amine content in the reaction mixture. Obtained amine terminated dendritic polymer of polyester type is then recovered by evaporating residual monomer and solvent by applying full vacuum to the reactor.

#### Examples 13-17

Examples 13-17 illustrate the use of the present dendritic polymer in a typical isocyanate-based high resilience (HR) based foam. In each Example, the isocyanate-based foam was prepared by the pre-blending of all resin ingredients including polyols, copolymer polyols (if used), catalysts, water, and surfactants as well as the dendritic macromolecule of interest (if used). The isocyanate was excluded from this mixture. The resin blend and isocyanate were then mixed at an isocyanate index of 100 using a conventional two-stream mixing technique and dispensed into a preheated mold (65°C) having the dimensions 38.1 cm x 38.1 cm x 10.16 cm. The mold was then closed and the reaction allowed to proceed until the total volume of the mold was filled. After approximately 6 minutes, the isocyanate-based foam was removed and, after proper conditioning, the properties of interest were measured. This methodology will be referred to in Examples 13-17 as the General Procedure.

In Examples 13-17, the following materials were used:

E837, base polyol, commercially available from Lyondell;

E850, a 43 % solids content copolymer (SAN) polyol, commercially available from Lyondell;

HBP, a dendritic macromolecule produced in Example 4 above;

DEAO LF, diethanolamine, a cross-linking agent commercially available from Air Products;

Glycerin, a cross-linking agent, commercially available from Van Waters & Rogers;

5 Water, indirect blowing agent;

Dabco 33LV, a gelation catalyst, commercially available from Air Products;

Niax A-1, a blowing catalyst, commercially available from Witco;

Y-10184, a surfactant, commercially available from Witco; and

Lupranate T80, isocyanate (TDI), commercially available from BASF.

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Unless otherwise stated, all parts reported in Examples 13-17 are parts by weight.

In Examples 13-15, isocyanate-based foams based on the formulations shown in Table 1 were produced using the General Procedure referred to above.

15 In Examples 13-15, isocyanate based foams were prepared in the absence of any copolymer polyol. The isocyanate-based foams were formulated with a % H<sub>2</sub>O concentration of 3.8% resulting in an approximate foam core density of 31 kg/m<sup>3</sup>. The level of the dendritic macromolecule was varied from 6.68% to 13.35% by weight in the resin.

20 The results of physical property testing are reported in Table 1. Also reported in Table 1 for each foam is the density and Indentation Force Deflection (IFD) at 50% deflection, measured pursuant to ASTM D3574. As shown, the introduction of the dendritic macromolecule to the isocyanate-based polymer matrix resulted in a ~98 N hardness increase for foam from Example 13 to Example 14, and a ~83 N hardness increase for the foam from Example 14 to Example 15.

25 By this analysis, a "load efficiency" for each foam may be reported and represents the ability of the dendritic macromolecule to generate firmness in the isocyanate based foam matrix. The load efficiency is defined as the number of Newtons of foam hardness increase per % of the dendritic macromolecule in the resin blend. The term "load efficiency", as used throughout this specification, is intended to have  
30 the meaning set out in this paragraph.



As shown, the introduction of the dendritic macromolecule resulted in a foam hardness increase of 181N. The resulting load efficiency is 27N/% dendritic macromolecule in the resin.

5 In Examples 16 and 17, isocyanate-based foams based on the formulations shown in Table 2 were produced using the General Procedure referred to above.

In Examples 16 and 17, isocyanate based foams were prepared in the absence of any dendritic macromolecule and used only copolymer polyol as the method by which foam hardness is increased. Thus, it will be appreciated that Examples 16 and 17 are provided for comparative purposes only and are outside the scope of the present  
10 invention. The isocyanate-based foams were formulated with a %H<sub>2</sub>O concentration of 3.8% resulting in an approximate foam core density of 31 kg/m<sup>3</sup>. The level of the copolymer polyol was varied from 26% to 8% by weight in the resin.

The results of physical property testing are reported in Table 2. As shown, the introduction of the copolymer polyol resulted in a foam hardness increase of 192.1 N.  
15 The resulting load efficiency is 10.69 N/% copolymer polyol in the resin. As will be apparent, this is significantly less than the load efficiency achieved in the foams produced in Examples 13-15.

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Table 1

Ingredient	Example		
	13	14	15
E837	92.8	89.2	85.6
E850	-	-	-
HBP	7.2	10.8	14.4
DEOA LF	1.1	1.1	1.1
Glycerin	0.6	0.6	0.6
H <sub>2</sub> O	3.93	3.93	3.93
Dabco 33LV	0.411	0.452	0.492
Niav A-1	0.08	0.08	0.08
Y10184	1	1	1
Total resin	107.12	107.16	107.2
Lupranate T80	51.737	53.197	54.658
Index	100	100	100
% H <sub>2</sub> O	3.8	3.8	3.8
% SAN in resin	0	0	0
% HBP in resin	6.68	10.01	13.35
Total dry weight (g)	476	471	473
Density (kg/m <sup>3</sup> )	31	31	31
50% IFD (N)	301.6	399.9	482.6
% Hysteresis	34.9	39.3	42.6
Load Efficiency	27.13		

Table 2

Ingredient	Example	
	16	17
E837	34.85	79.95
E850	65.15	20.05
HBP	-	-
DEOA LF	1.1	1.1
Glycerin	0.6	0.6
H <sub>2</sub> O	3.93	3.93
Dabco 33LV	0.33	0.33
Niax A-1	0.08	0.08
Y10184	1	1
Total resin	107.04	107.04
Lupranate T80	40.817	41.432
Index	100	100
% H <sub>2</sub> O	3.8	3.8
% SAN in resin	26	8
% HBP in resin	0	0
Total dry weight (g)	550	556
Density (kg/m <sup>3</sup> )	31	31
50% IFD (N)	468.4	276.3
% Hysteresis	38.4	29.1
Load Efficiency	10.69	

While this invention has been described with reference to illustrative embodiments and examples, the description is not intended to be construed in a limiting sense. For example, while esterification/acid derivatization and ring-opening techniques were used in some of the Examples to produce embodiments of the novel dendritic macromolecules, other derivatization techniques such as transesterification, polyaddition reactions, free radical polymerization and the like can be used. Thus, various modifications of the illustrative embodiments, as well as other embodiments of the invention, will be apparent to persons skilled in the art upon reference to this description. It is therefore contemplated that the appended claims will cover any such modifications or embodiments.

All publications, patents and patent applications referred to herein are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

What is claimed is:

1. A dendritic macromolecule having the following characteristics:
  - (i) an active hydrogen content of greater than about 3.8 mmol/g;
  - (ii) an active hydrogen functionality of at least about 8; and
  - (iii) at least a 15% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number less than about 40 mg KOH/g to form a stable liquid at 23°C.
2. The dendritic macromolecule defined in claim 1, wherein from about 15% to about 30% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number less than about 40 mg KOH/g to form a stable liquid at 23°C
3. The dendritic macromolecule defined in claim 1, wherein at least a 15% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number in the range of from about 25 to 35 mg KOH/g to form a stable liquid at 23°C.
4. The dendritic macromolecule defined in claim 1, wherein at least a 15% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number in the range of from about 28 to 32 mg KOH/g to form a stable liquid at 23°C.
5. The dendritic macromolecule defined in any one of claims 1-4, wherein the active hydrogen is present in the macromolecule in the form of one or more mercapto moieties.
6. The dendritic macromolecule defined in any one of claims 1-4, wherein the active hydrogen is present in the macromolecule in the form of one or more primary amino moieties.

7. The dendritic macromolecule defined in any one of claims 1-4, wherein the active hydrogen is present in the macromolecule in the form of one or more secondary amino moieties.

8. The dendritic macromolecule defined in any one of claims 1-4, wherein the active hydrogen is present in the macromolecule in the form of one or more hydroxyl moieties.

9. The dendritic macromolecule defined in any one of claims 1-4, wherein the active hydrogen is present in the macromolecule in the form of two or more of a mercapto moiety, a primary amino moiety, a secondary amino moiety and a hydroxyl moiety.

10. The dendritic macromolecule defined in any one of claims 1-9, wherein the active hydrogen content of the macromolecule is in the range of from about 3.8 to about 10 mmol/g.

11. The dendritic macromolecule defined in any one of claims 1-9, wherein the active hydrogen content of the macromolecule is in the range of from about 3.8 to about 7.0 mmol/g.

12. The dendritic macromolecule defined in any one of claims 1-9, wherein the active hydrogen content of the macromolecule is in the range of from about 4.4 to about 5.7 mmol/g.

13. The dendritic macromolecule defined in any one of claims 1-12, wherein the active hydrogen functionality in the macromolecule is in the range of from about 8 to about 70.

14. The dendritic macromolecule defined in any one of claims 1-12, wherein the active hydrogen functionality in the macromolecule is in the range of from about 10 to about 60.

15. The dendritic macromolecule defined in any one of claims 1-12, wherein the active hydrogen functionality in the macromolecule is in the range of from about 15 to about 35.

16. The dendritic macromolecule defined in any one of claims 1-12, wherein the active hydrogen functionality in the macromolecule is in the range of from about 20 to about 30.

17. The dendritic macromolecule defined in any one of claims 1-16, wherein from about 15% to about 50% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number less than about 40 mg KOH/g to form a stable liquid at 23°C

18. The dendritic macromolecule defined in any one of claims 1-16, wherein from about 15% to about 40% by weight of the dendritic macromolecule may be mixed with a polyether polyol having an OH number less than about 40 mg KOH/g to form a stable liquid at 23°C.

19. The dendritic macromolecule defined in any one of claims 1-18, wherein the macromolecule has an inherently branched structure comprising at least one of an ester moiety, an ether moiety, an amine moiety, an amide moiety and any mixtures thereof.

20. The dendritic macromolecule defined in any one of claims 1-18, wherein the macromolecule has an inherently branched structure comprising primarily an ester moiety, optionally combined with an ether moiety.

21. The dendritic macromolecule defined in any one of claims 1-18, wherein the macromolecule has an inherently branched structure comprising primarily an ether moiety, optionally combined with an ester moiety.

22. The dendritic macromolecule defined in any one of claims 1-18, wherein the macromolecule has an inherently branched structure comprising primarily an ester moiety, optionally combined with an ether moiety.

23. The dendritic macromolecule defined in any one of claims 19-22, further comprising a nucleus to which the inherently branched structure is chemically bonded.

24. The dendritic macromolecule defined in any one of claims 19-22, wherein a plurality of inherently branched structures are chemically bonded to one another.

25. The dendritic macromolecule defined in any one of claims 19-24, wherein the inherently branched structure further comprises at least one chain stopper moiety chemically bonded thereto.

26. The dendritic macromolecule defined in any one of claims 19-24, wherein the inherently branched structure further comprises at least two different chain stopper moieties chemically bonded thereto.

27. The dendritic macromolecule defined in any one of claims 19-26, wherein the inherently branched structure further comprises at least one spacing chain extender chemically bonded thereto.

28. The dendritic macromolecule defined in claim 27, wherein the spacing chain extender is monomeric.

29. The dendritic macromolecule defined in claim 27, wherein the spacing chain extender is polymeric.



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less than about 85% by weight a polyether polyol having an OH number less than about 40 mg KOH/g.

32. The composition of matter defined in claim 30, wherein the dendritic macromolecule is present in an amount in the range of from about 30% to about 50% by weight.

33. The composition of matter defined in claim 30, wherein the dendritic macromolecule is present in an amount in the range of from about 35% to about 45% by weight.

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(iii) at least a 15% by weight of the dendritic macromolecule may be mixed

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Dendritic polymer addition level [wt %]	Example 6 Viscosity [mPas]	Example 4 Viscosity [mPas]	Example 5 Viscosity [mPas]
0	~1000	~1000	~1000
10	~2000	~2500	~2500
15	~3000	~4000	~5000
20	~4000	~4500	~14000
25	~5000	~6000	~26000
30	~6000	~9000	-
40	~17000	~22000	-
50	~31000	-	-

**Figure**